Performance enhancement of diammonium hydrogen phosphate as halogen and formaldehyde free sustainable fire retardant

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REZUMAT – ABSTRACT

Îmbunătățirea performanței hidrogenofosfatului de diamoniu ca ignifugant durabil fără halogen și formaldehidă

Ignifuganții pe bază de fosfor sunt utilizați în general pentru a conferi un caracter ignifug țesăturii de bumbac. Cu toate acestea, majoritatea ignifuganților eficienți pe bază de fosfor pentru textile conțin halogen toxic și/sau formaldehidă. Hidrogenofosfatul de diamoniu nu conține halogen sau formaldehidă, dar performanța sa este mult mai mică decât a substanțelor ignifuge disponibile în comerț. Prin urmare, în acest studiu, hidrogenofosfatul de diamoniu a fost polimerizat cu agenți de reticulare fără conţinut de formaldehidă, cum ar fi acidul acrilic și acidul maleic. Concentrațiile de monomeri și inițiatori, condițiile de polimerizare și temperatura au fost optimizate. Țesătura tratată pe baza noii rețete a prezentat performanțe bune de ignifugare, precum și proprietăți suplimentare ale controlului contracției, îngrijire ușoară și proprietăți antimicrobiene. Testarea analitică SEM, FTIR și a conținutului de fosfor a confirmat, de asemenea, aplicarea cu succes a finisajului.

Cuvinte-cheie: ignifugant, finisare cu îngrijire ușoară, controlul contracției, antimicrobian, sare de fosfat

Performance enhancement of diammonium hydrogen phosphate as halogen and formaldehyde free sustainable fire retardant

Phosphorous based fire retardants are commonly used for imparting fire retardancy to the cotton fabric. However, most of theeffective phosphorous based fire retardants for textile contain toxic halogen and/or formaldehyde. Diammonium hydrogen phosphate does not contain halogen or formaldehyde but its performance is far less than the commercially available fire retardants. Therefore, in this research Diammonium hydrogen phosphate was polymerized with zero formaldehyde based cross-linkers like acrylic acid and maleic acid. Concentrations of monomers and initiator, polymerization conditions and temperature were optimized. Newly developed recipe treated fabric exhibited good fire retardancy performance as well as additional properties of shrinkage control, easy care and anti-microbial. Analytical testing of SEM, FTIR and phosphorous content also confirmed the successful application of the finish.

Keywords: fire retardant, easy carefinishing, shrinkage control, anti-microbial, phosphate salt

INTRODUCTION

Fire play vital role in our lives. However, it is very dangerous when out of control. Over 0.3 million people die andmany more get injured while billions of loss in property is reported every year due to fire breakout. According to fire hazard statistics of United State of America 2015, the fire department has responded to an estimated 1,345,500 fire incidents; over 1570 civilians died during these fire incidents and 14.3 billion dollar direct property loss was reported [1–2]. Carpets, upholstery and most importantly textile apparel are the last barrier for fire before it can cause harm to humans. Therefore, fire retardant chemicals consumption are increasing and it was worth more than 5.6 billion pounds in 2017. There is no doubt that cotton is the most widely used natural fiber but it lacks fire retardancy, in fact it will spread more fire once ignited [3–5].

It is unfortunate that the most widely used fire retardants for textile like Pyrovatex CP New (modified N-methyloldimethylphosphonopropionamide) and THPC (Tetrakishydroxymethylphosphonium chloride) are not environment friendly. Pyrovatex contain carcinogenic formaldehyde while THPC required non-conventional and non-environment friendly ammonia chamber [6–9].

Zero discharge of hazardous chemicals (ZDHC) program, vision 2020 and its signatory brands have included the conventional effective halogenated fire retardants in their 11 banned priority chemicals. In addition, certifications for organic textile products also prohibit the use of halogen and formaldehyde based fire repellents. Therefore, researchers are working on finding the effective alternatives. Ammonium phosphate salts are one such alternative [10] but its performance is far less than the commercial Pyrovatex and THPC. Carboxylic acids are good alternative for formaldehyde based cross-linkers [11–14]. Researchers have reported the use of butane tetra carboxylic acid (BTCA) as fire retardant enhancer with Pyrovatex but BTCA is very expensive and

Pyrovatexitself is toxic. Certain cost effective carboxylic acids like maleic acid (di carboxylic acid) with C6 fluorocarbon has been reported as oil and water repellent [15] while acrylic acid (mono carboxylic acid) as surface modifier for textile fabric.

Diammonium hydrogen phosphate (DAHP) has been reported as environment friendly, non-toxic and cost effective fire retardant for textile. However, its performance is much less than the commercially available products. Researchers have reported the use of melamine formaldehyde [16] as enhancer with DAHP but melamine formaldehyde contains carcinogenic formaldehyde. In this research DAHP is polymerized withformaldehyde freecross-linkers; maleic acid and acrylic acid under normal atmosphere and nitrogen atmosphere at various conditions. The performance of the newly polymerized recipes was assessed on the cotton fabric.

EXPERIMENTAL WORK

Materials and methods

In this research 100% cottonbleached fabric with 280 GSM was used. Following lab grade chemicals; Diammonium hydrogen phosphate (DAHP), sodium hypophosphite (SHSP), acrylic acid, potassium per sulfate (PPS) and maleic acid were purchased from Sigma Aldrich.

Methods

In this research non-toxic and formaldehyde free cross-linkers like acrylic acid and maleic acid have been used along with halogen free fire retardant monomer; diammonium hydrogen phosphate (DAHP). Concentrations of DAHP and cross-linkers as well as temperature of polymerization were optimized. The polymerization time was optimized for one hour. Potassium per sulfate was used as initiator and sodium hypophosphite as catalyst. The polymerized recipe was applied through padding by using 80% pick up. Drying was carried out at hundred degrees for three minutes while curing was performed at one hundred and eighty degrees for two minutes. All the samples were conditioned at 65% relative humidity and 20°C prior to any testing. Limiting oxygen index was assessed by the standard method of ASTM D 2863. BS 5438: 1989, Test 2B vertical burning test was performed to measure the damaged char length and width. Crease recovery and shrinkage were assessed by using BS EN 22313: 1992 and AATCC test method 135: 2004 respectively. AATCC 147 test method was performed to determine the antimicrobial performance. The air permeability was measured by using method D737: 1996. Olsen method [17] was used to measure the concentration of phosphorous. FTIR was also performed for samples with 32 background scan and from wave number range of 650 to 4000 cm^{-1}.Gold coating treatment was carried out before performing SEM analysis.

RESULTS AND DISCUSSIONS

Untreated control cotton fabric was burnt immediately and completely. One of the most commonly used fire retardant for textile, Pyrovatex, has been used as bench mark in this study. Manufacturer suggested recipe of 20% Pyrovatexalong with 1.5% of formaldehyde based trimethylol melamine catalyst CHN and 2.5% of phosphoric acid was applied on to the treated fabric. The treated samples have exhibited the char length of 98 mm and char width of 32 mm (table 1). By raising the quantity of Pyrovatex from 20% to 40% there was further improvement in the fire retardancy, consequently, char length and width of 64 mm and 28 mm respectively were obtained (table 1). Performance of the diammonium hydrogen phosphate (DAHP) was also assessed at the level of 5%, 10%, 20% and 40%. Char length and width were reduced by increasing the quantity of DAHP. The reduction in char length and width is higher at low levels of DAHP and slowed down after 20% due to saturation effect.

Table 1

FIRE RETARDANCY OF PYROVATEX AND DIAMMONIUM HYDROGEN PHOSPHATE TREATED COTTON

Fire retardant chemical	Catalyst/ Cross-linker	Char length (mm)	Char width (mm)
Control fabric	-	Complete burn	Complete burn
Pyrovatex, 20%	Phosphoric acid 2.5%, Catalyst (CHN) 1.5%	98	32
Pyrovatex, 40%	Phosphoric acid 6%, Catalyst (CHN) 2.2%	64	28
DAHP, 5%	-	184	46
DAHP, 10%	-	142	41
DAHP, 20%	-	101	32
DAHP, 40%	-	95	28

Preparation of fire retardant and its application to the cotton fabric

The cotton fabric treated with maleic acid was burnt completely and did not show any kind of fire retardancy. Table 2 represent the results of polymerization at normal atmosphere. Increasing the polymerization temperature from 25°C to 120°C exhibited reduction in the char length. Nevertheless, polymerization temperature greater than 120°C imparted no improvement.

Alone acrylic acid treated cotton fabric was also burnt completely. Table 3 exhibited the results of polymerization between DAHP and acrylic acid where atmosphere is not controlled. In the case of acrylic acid polymerization with DAHP the char length was decreased by raising the temperature from 25°C to 90°C and after that there was no improvement.

Table 2

EFFECT OF TEMPERATURE ON POLYMERIZATION OF MALEIC ACID AT NORMAL ATMOSPHERE				
Fire retardant chemical DAHP (%)	**Cross linker Maleic acid (%)**	**Polymerization temperature (°C)**	**Char length (mm)**	**Char width (mm)**
-	5	-	Complete burn	Complete burn
-	10	-	Complete burn	Complete burn
-	15	-	Complete burn	Complete burn
10	10	25	136	41
10	10	80	129	36
10	10	100	126	33
10	10	120	119	33
10	10	140	119	33
10	10	160	134	37

Table 3

EFFECT OF TEMPERATURE ON POLYMERIZATION OF ACRYLIC ACID AT NORMAL ATMOSPHERE				
Fire retardant chemical DAHP (%)	**Cross linker Acrylic acid (%)**	**Polymerization temperature (°C)**	**Char length (mm)**	**Char width (mm)**
-	5	-	Complete burn	Complete burn
-	10	-	Complete burn	Complete burn
-	15	-	Complete burn	Complete burn
10	10	25	129	33
10	10	50	116	31
10	10	75	102	31
10	10	90	70	30
10	10	100	72	30

Typically, lot of side reactions can take place under atmospheric conditions. In addition, nitrogen in combination with phosphorous can improve the fire retardancy of the fabric. Therefore, polymerization was also performed in nitrogen atmosphere. Improved fire retardancy was achieved when polymerization was carried out under nitrogen atmosphere with DAHP and maleic acid. The minimum char length and width was achieved at the polymerization temperature of 120°C (table 4).

Similarly, acrylic acid was also polymerized with DAHP in nitrogen atmosphere. The minimum burnt char length and width was observed at 90°C as shown in table 5. Similarly the improvement in the char length and width can easily be noticed when the polymerization was carried out under nitrogen atmosphere as compared to normal atmosphere.

Diammonium hydrogen phosphate was polymerized with maleic acid and acrylic acid without catalyst and initiator, with catalyst and without initiator, with catalyst and initiator under nitrogen atmosphere at 120°C and 90°C respectively as shown in table 6. Potassium per sulfate was also used in polymerization because it is a well-known initiator. In addition, sodium hypophosphite has been reported as catalyst for carboxylic acids [11], consequently, it was used in the

Table 4

EFFECT OF TEMPERATURE ON POLYMERIZATION OF MALEIC ACID UNDER NITROGEN ATMOSPHERE				
Fire retardant chemical DAHP (%)	**Cross linker Maleic acid (%)**	**Polymerization temperature (°C)**	**Char length (mm)**	**Char width (mm)**
10	10	25	113	36
10	10	80	109	34
10	10	100	95	33
10	10	120	85	21
10	10	140	90	25
10	10	160	91	24

Table 5

EFFECT OF TEMPERATURE ON POLYMERIZATION OF ACRYLIC ACID UNDER NITROGEN ATMOSPHERE				
Fire retardant chemical DAHP (%)	**Cross linker Acrylic acid (%)**	**Polymerization temperature (°C)**	**Char length (mm)**	**Char width (mm)**
10	10	25	88	39
10	10	50	97	30
10	10	75	68	28
10	10	90	26	27
10	10	100	39	28

Table 6

EFFECT OF CATALYST AND INITIATOR ON POLYMERIZATION UNDER NITROGEN ATMOSPHERE							
Fire retardant chemical	**Cross linker**	**Cross linker**	**Catalyst**	**Initiator**	**Polymerization temperature (°C)**	**Char length (mm)**	**Char width (mm)**
DAHP (%)	Maleic acid (%)	Acrylic acid	Sodium hypophosphite (%)	Potassium per sulfate (%)			
10	10	-	-	-	120	85	21
10	10	-	8	-	120	81	19
10	10	-	8	0.01	120	66	19
10	10	-	8	0.02	120	39	16
10	10	-	8	0.03	120	43	22
10	-	10		-	90	26	27
10	-	10	8	-	90	25	27
10	-	10	8	0.1	90	19	26
10	-	10	8	0.2	90	15	25
10	-	10	8	0.3	90	16	25

polymerization. The most effective results were obtained with catalyst and initiator. The optimum amount of potassium per sulfate was 0.02% as exhibited in table 6. Therefore, sodium hypophosphite and potassium per sulfate were used as catalyst and initiator respectively in the remaining research.

The diammonium hydrogen phosphate was polymerized with maleic acid and acrylic acid under nitrogen atmosphere with catalyst and initiator at optimum temperature with various levels of DAHP, maleic acid and acrylic acidas shown in table 7. The optimum results were achieved when 10% diammonium hydrogen

Table 7

EFFECT OF CONCENTRATION OF FIRE RETARDANT MONOMER AND CROSS-LINKER AT OPTIMUM TEMPERATURE WITH CATALYST AND INITIATOR UNDER NITROGEN ATMOSPHERE							
Fire retardant chemical	**Cross linker**	**Cross linker**	**Catalyst**	**Initiator**	**Polymerization temperature (°C)**	**Char length (mm)**	**Char width (mm)**
DAHP (%)	Maleic acid (%)	Acrylic acid	Sodium hypophosphite (%)	Potassium per sulfate (%)	-	-	-
10	5	-	8	0.01	120	53	24
10	10	-	8	0.02	120	39	16
10	15	-	8	0.03	120	40	17
5	10	-	8	0.02	120	83	39
10	10	-	8	0.02	120	39	16
15	10	-	8	0.02	120	38	16
10	-	5	8	0.1	90	21	25
10	-	10	8	0.2	90	15	25
10	-	15	8	0.3	90	33	30
5	-	10	8	0.2	90	49	36
10	-	10	8	0.2	90	15	25
15	-	10	8	0.2	90	17	26

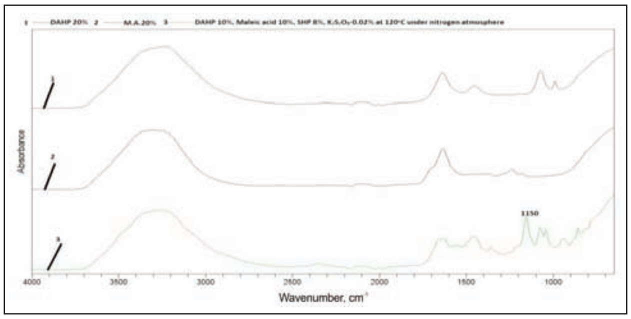


Fig. 1. FTIR analysis with maleic acid recipe

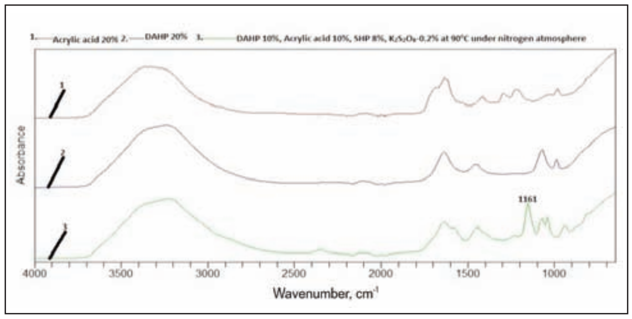


Fig. 2. FTIR analysis with acrylic acid recipe

phosphate was polymerized with 10% maleic acid, 8% sodium hypophosphite and 0.2% potassium per sulfate. Similar conditions were repeated with 10% acrylic acid as well.

FTIR analysis were performed on the range of recipes; DAHP (20% solution in water), maleic acid (20% solution in water) and best polymerized recipe with maleic acid as shown in figure 1. FTIR were also performed on acrylic acid (20% solution in water) and best polymerized recipe with acrylic acid, figure 2. The optimized recipes in case of maleic acid and acrylic acid along with DAHP, sodium hypophosphite, potassium per sulphate at 120° under nitrogen atmosphere exhibited the prominent ester peaks at 1150 cm^{-1} and 1161 cm^{-1} respectively. Consequently, formation of effective ester bonding can be confirmed from the FTIR analysis. P-O-C stretch has been exhibited at the 920–1088 cm^{-1} for DAHP and best recipe either with maleic acid or acrylic acid, however, no such peak can be observed for alone maleic acid or acrylic acid.

Physical and mechanical properties of cotton fabric

Measurement of fire retardancy through objective testing like limiting oxygen index (LOI) % is also important. Therefore, LOI % of the selected samples was also performed. More the percentage of LOI better will be the fire retardancy. LOI of the control fabric was 18.1% indicating that it will easily catch the fire. Similarly, the maleic acid (20%) and acrylic acid (20%) treated fabric imparted the LOI% of 18.2%, demonstrating that there is hardly any improvement in the fire retardancy of the treated fabric when both carboxylic acids are used. The benchmark sample of 40% Pyrovatex treated fabric exhibited good LOI% of 34.1%. 20% DAHP treated fabric exhibited LOI% of 24.1. In case of cotton fabric treated with 10% maleic acid along with 10% diammonium hydrogen phosphate, 8% sodium hypophosphite, 0.2% potassium per sulfate the best LOI reported was 29.1%. However, the highest LOI% of 34.8% was achieved when cotton fabric was treated with 10% acrylic acid, 10% DAHP, 8% sodium hypophosphite and 0.2% potassium per sulfate. It can easily be said from tables 7 & 8 that both char length-width and LOI% demonstrated similar trends.

Spread of fire through smoldering cigarette is very common all around the world. Therefore, smoldering cigarette test is performed on the cotton fabric samples. It was noticed as expected that control cotton fabric burnt easily. 40% Pyrovatextreated fabric was burnt in significant high time of 31 minutes. The highest burnt time of 32 minutes was achieved for the cotton fabric treated with DAHP 10%,acrylic acid 10%, catalyst 8% and initiator 0.02% (table 8).

Cotton fabric lacks the easy care properties and demonstrated the low crease recovery angle (table 8). It is mainly due to more amorphous region around 30% in the cotton as well as weak hydrogen bonding. Maleic acid and acrylic acid are both cross-linkers and consequently improved the bonding of the cellulose chains, therefore crease recovery is improved as compared to control cotton fabric. DAHP is not an effective cross-linker, therefore, improvement was minimal. However, crease recovery angle was significantly increased when DAHP10% with maleic acid 10%, catalyst 8% and initiator 0.2% were applied onto the fabric after the polymerization at 120°C under nitrogen atmosphere (table 8). It can also be concluded that due to new recipe effective bonding with the treated fabric, there was improvement in the fire retardancy and crease recovery angle.

One of the advantages of cotton fabric is its good air permeability. Therefore, control fabric air permeability is set as 100%. Maleic acid, acrylic acid and DAHP exhibited slight decrease in the air permeability as these chemical coating on the cotton fabric will prevent the air permeability. Pyrovatex at the higher level of 40% exhibited the least air permeability retention of 69% due to more sever coating onto the cotton fabric at high dosage. The best recipe of maleic acid along with DAHP and others exhibited the reasonable air permeability retention of 86%.

As mentioned above that cotton has amorphous region as well as weak hydrogen bonding, consequently, cotton fabric demonstrated shrinkage after washing due to lack of strong forces. However, maleic acid and acrylic acid treated fabric exhibited good shrinkage control due to the cross-linking of the cellulose chains. It was also not surprising that the best recipe of maleic acid along with DAHP, catalyst and initiator exhibited the best shrinkage control results due to their effective cross-linking.

Fire retardant finish performance can be determined through its phosphorous content as well. Therefore,

Table 8

LOI% OF VARIOUSFIRE RETARDANTS						
Sample type	**Limiting oxygen index (%)**	**Crease recovery angle (degree)**	**Air permeability (% retention)**	**Shrinkage of fabric in warp direction (%)**	**Shrinkage of fabric in weft direction (%)**	**Smoldering cigarette test results (minutes)**
Control fabric	18.1	137	100	7.6	6.2	11
Maleic acid	18.2	208	91	2.2	1.1	12
Acrylic acid	18.2	205	91	2.2	1.1	11
DAHP	24.1	141	88	3.4	2.1	14
Pyrovatex 20%	27.5	168	85	3.7	3.2	17
Pyrovatex 40%	34.1	179	69	2.8	2.4	31
DAHP 10% + Maleic acid 10% at 120°C under nitrogen atmosphere	24.8	195	87	2.1	1.6	15
DAHP 10% + Acrylic acid 10% at 90°C under nitrogen atmosphere	25.1	189	88	2.1	1.6	16
DAHP 10% + Maleic acid 10% + SHP 8% + $K_2S_2O_8$ 0.2% at 120°C under nitrogen atmosphere	29.1	211	86	1.7	1.2	30
DAHP 10% + Acrylic acid 10% + SHP 8% + $K_2S_2O_8$ 0.2% at 90°C under nitrogen atmosphere	34.8	208	86	1.8	1.2	32

phosphorous content of the various fire retardant finishes were assessed. It was not surprising that distilled water, maleic acid and acrylic acid recipes exhibited no phosphorous content. Highest phosphorus content was achieved for 40% Pyrovatex treated fabric. Normally, 17,000 ppm is considered enough for imparting fire retardancy. The best recipe of maleic acid, DAHP, catalyst and initiator exhibited good phosphorous content of 31,350 ppm demonstrating the effectiveness of the finish (table 9).

The development of formaldehyde free fire retardant was the basic purpose of this research, therefore, formaldehyde content of the various finished fabric was assessed. Pyrovatex treated fabric exhibited the formaldehyde content confirming the presence of toxic formaldehyde in the treated fabric. However, no formaldehyde was detected in any of the fabric treated with maleic acid, acrylic acid and DAHP combination, thus confirming that the newly developed recipes are completely formaldehyde free (table 10).

Surface morphology of finished cotton fabric

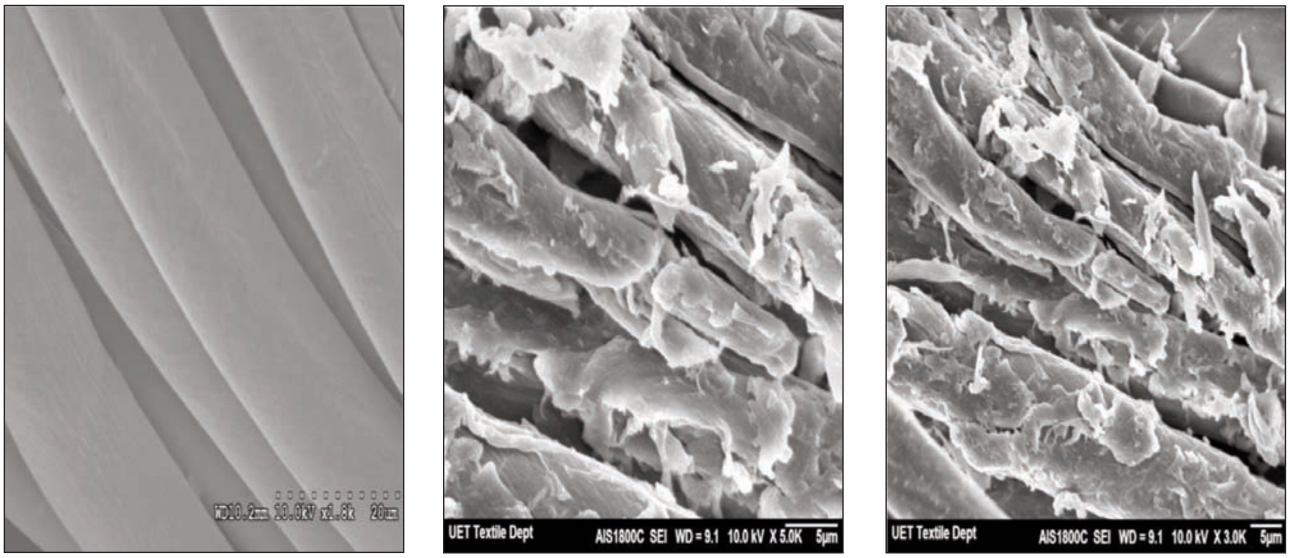
The surface of the control cotton fabric was smooth and clean as evident from the image of scanning electron microscope (SEM), (figure 3, *a*). However, there was confirmation of the coating on the surface of the cotton fabric when it was treated with recipe containing DAHP10%, maleic acid 10%, catalyst 8%

Table 9

PHOSPHOROUS CONCENTRATION IN VARIOUS FIRE RETARDANTS	
Item Name	**Concentration of phosphorous (ppm)**
Distilled water	0
Maleic acid 10%	0
Acrylic acid 10%	0
DAHP 10%	27,367.2
Pyrovatex 20%	17,689.7
Pyrovatex 40%	43,344.8
Maleic acid 10% + DAHP 10% + SHP 8% + $K_2S_2O_8$ 0.2% polymerized at 120°C under nitrogen atmosphere	31,350.72
Acrylic acid 10% + DAHP 10% + SHP 8% + $K_2S_2O_8$ 0.2% polymerized at 90°C under nitrogen atmosphere	31,378.18

Table 10

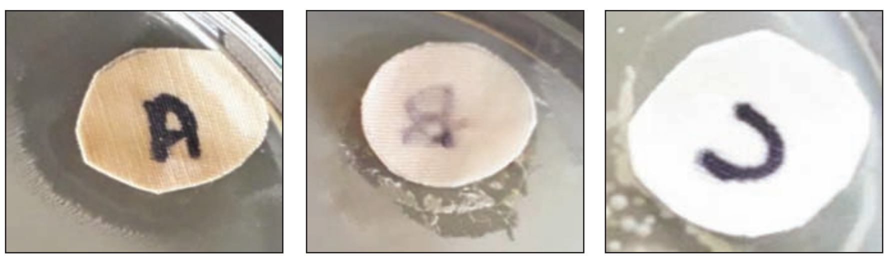
FORMALDEHYDE CONTENT IN FABRIC	
Item Name	**Formaldehyde content in fabric (ppm)**
DAHP 10%	0
Pyrovatex 20%	32
Pyrovatex 40%	41
Maleic acid 10% + DAHP 10% + SHP 8% + $K_2S_2O_8$ 0.2% polymerized at 120°C under nitrogen atmosphere	0
Acrylic acid10% + DAHP 10% + SHP 8% + $K_2S_2O_8$ 0.2% polymerized at 90°C under nitrogen atmosphere	0



a *b* *c*

Fig. 3. SEM images of: *a* – Untreated, *b* – DAHP 10% + Maleic acid 10% + SHP 8% + $K_2S_2O_8$ 0.2% at 120°C under nitrogen atmosphere, *c* – DAHP 10% + Acrylic acid 10% + SHP 8% + $K_2S_2O_8$ 0.2% at 90°C under nitrogen atmosphere

and initiator 0.2% (figure 3, *b*). The figure 3, *c* exhibited the result when best recipe was applied on cotton fabric with respect to acrylic acid, DAHP, catalyst and initiator. Figures 3, *b* and 3, *c* confirmed the successful application of the both recipes onto the treated cotton fabric.



a *b* *c*

Fig. 4. *a* – DAHP 10% + Acrylic acid 10% + SHP 8% + Potassium per sufate 0.5% at 90°C under nitrogen atmosphere, *b* – DAHP 10% + Maleic acid 10% + SHP 8% + Potassium per sulfate 0.2% at 120°C under nitrogen atmosphere, *c* – untreated

Antimicrobial performance of finished cotton fabric

It is quite well know that cotton is easily attacked by the microbes and same is demonstrated in our tests (figure 4, *c*). Both of the carboxylic acids; maleic acid and acrylic acid along with DAHP, catalyst and initiator treated fabric exhibited antimicrobial properties and clear zone of inhabitation of 0.20 mm and 0.82 mm respectively.

CONCLUSION

Halogen and formaldehyde free flame retardant have been synthesized by using the diammonium hydrogen phosphate and carboxylic acids like maleic acid and acrylic acid. The optimum results with respect to flame retardancy like limiting oxygen index and vertical burning were achieved when polymerization was carried out under nitrogen atmospherewith $K_2S_2O_8$ 0.2%, sodium hypophosphite 8%, diammonium hydrogen phosphate 10% along with maleic acid 10% and acrylic acid 10% at 120°C and 90°C respectively. There was also improvement in the burnt time of the smoldering cigarette test.

Important additional properties of antimicrobial, crease recovery and better shrinkage control have been demonstrated by the optimum recipes. The successful synthesis and application of the newly recipes were confirmed by the FTIR analysis, phosphorous content and SEM analysis.

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